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THERMOELECTRIC BONDING STUDY

First Quarterly Progress Report

Covering the Period from

29 June to 30 September 1964

October 27, 1964

Prepared for
National Aeronautics and Space Administration
Goddard Space Flight Center

HITTMAN ASSOCIATES, INC.
BALTIMORE, MARYLAND

LEGAL NOTICE

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FOREWORD

This report covers the work accomplished during the period 29 June to 30 September 1964 under Contract NAS5-3973.

I. INTRODUCTION

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This program encompasses an investigation of the bonding of lead telluride to shoe materials to form thermoelectric couples. The objective is to study the bonding process and to determine the mechanism or mechanisms of bond deterioration and failure in lead telluride thermoelectric elements. A secondary requirement is that the materials selected for shoes and brazes be non-magnetic, if possible.

The procedure followed to date is as follows:

1. A literature survey reviewing work in bonding PbTe at other installations was performed.
2. Potential braze and shoe materials were selected for evaluation.
3. As a preliminary test the wettability of PbTe and the selected shoe materials by each potential braze was determined.
4. The effect of small additions of various braze and shoe materials on the Seebeck coefficient and electrical resistivity of PbTe was determined.

Author

The work outlined above will be completed early in the next quarterly reporting period and bond preparation and evaluation will begin.

II. LITERATURE SURVEY

A survey of the technical literature was undertaken to study previous work in formation of element to shoe bonds in PbTe thermoelectric elements. Much of the earlier work was performed as part of module or generator programs and in these cases the objective was to find a satisfactory bond for a particular application. Two fairly detailed bonding studies were undertaken under Navy sponsorship by General Atomics(1) and Westinghouse(2).

At General Atomics(1) about fifteen alloys, mostly intermetallic compounds and eutectics, were tested as possible brazes for p- and n-type PbTe. Shoe materials were 0.005 inch thick sheets of iron, nickel, tin plated iron, tin plated nickel, and gold. Bonded specimens were checked for resistivity and were evaluated by life and cycling tests. Nickel shoes were generally superior to iron. A few couples bonded to gold shoes were unsatisfactory. Testing of bonded specimens had not been completed when the final report was prepared by GA. Tentative conclusions were that several bond-shoe combinations were promising for use with n-type PbTe, including:

SnTe on Sn plated Fe

AuTe on Sn plated Ni

PbSe on Fe

InSb on 321 Stainless Steel

Four bonded p-type PbTe samples were tested and all showed drastic property changes within 100 hours. Better results were achieved with PbSnTe p-material.

Westinghouse(2) found that NiP or 302 stainless steel sprayed on 302 stainless foil made satisfactory bonds to n-type PbTe. Best results with p-PbTe were achieved by bonding the telluride with NiP to NiP coated gold foil. However, the expansion mismatch required that the gold deform, thereby limiting the thickness of foil. Earlier, as part of the Module Improvement Program, Westinghouse(3) had successfully tested two PbTe couples that were pressure bonded to iron hot straps and tin brazed to the cold shoe. The number of unsatisfactory modules was not reported.

Martin[4] and Tyco[5] reported some success with SnTe braze material, but GE[6] attempted to apply the Tyco process and observed deterioration of properties within a few hours.

Martin[4] and General Instrument[7] achieved some success with tin brazed contacts, particularly on the cold shoe.

DuPont[8] obtained satisfactory diffusion bonds between WSe_2 and p-type PbTe by heating under 150 psi to 500°C in 40% air - 60% Argon atmosphere.

Study of the literature is continuing as additional reports become available.

III. PREPARATION OF LEAD TELLURIDE ELEMENTS

Two types of lead telluride thermoelectric elements have been used to date in the performance of this program. Because of the need to incorporate additives in the elements as part of the poison effects study it was necessary to produce the PbTe elements from powders in our laboratory. Therefore, commercially available PbTe powders, types TEGS-2P and TEGS-2N, were procured from Minnesota Mining and Manufacturing Company (3M) for fabrication into elements by hot pressing.

For purposes of comparison and for checking out our Seebeck and resistivity test devices cold-pressed and sintered elements made from the same types of powder were purchased from 3M. In neither case would the vendor identify the dopants in these materials.

Lead telluride elements were fabricated by the following process. The correct amount of powder was weighed out. If a poison additive was included the weighed powders were placed in a glass bottle and tumble mixed for one hour. The PbTe or blended powder was then loaded into a single action graphite die. The die was placed into an inert atmosphere chamber which consisted of a nine inch cube of plexiglas. Lead-throughs were available for an induction coil, argon inlet and outlet and a piston through which the load was applied. The chamber was then purged with argon, heat was applied through a 5 Kw induction unit, the die was raised to temperature and the load was applied and held for 10 - 15 minutes.

Two sizes of PbTe elements were produced, 3/8 inch diameter by 5/8 inch high, and 1/2 inch diameter by 3/4 inch high. The optimum hot pressing conditions for these elements are given in Table I. About sixty pellets have been prepared to date. The elements appear to be sound and have densities in excess of 97 percent of theoretical. Metallographic examination indicates almost noporosity compared with extensive porosity in 3M cold-pressed and sintered elements.

TABLE I

Hot Pressing Conditions for PbTe Elements

Type	Diameter, inches	Load, tsi	Temperature, ^{o}C	Time at Pressure, Minutes
n-PbTe	3/8	1.25	744	15
p-PbTe	3/8	1.25	760	15
n-PbTe	1/2	1.25	788	10 - 15
p-PbTe	1/2	1.25	760	10 - 15

IV. BRAZE AND SHOE MATERIALS

A. Braze Alloys

Prospective braze alloys were selected on the basis of the following criteria:

1. Melting point below that of PbTe (917^{O}C).

2. Expectation that serious poisoning would not occur.

3. Expected remelt temperature above device operating temperature.

Other desirable criteria such as wettability and compatible coefficient of thermal expansion could not be applied because of a lack of reliable data. On the above basis the materials listed in Table II were selected for preliminary evaluation as braze materials. Those containing copper and silver, known poisons to PbTe, were selected for use as controls to check our instrumentation.

Metals for the preparation of braze alloys were procured from American Smelting and Refining Company, except for the pure tin which was purchased from Cominco Products, Incorporated. Each metal was 99. 999+ percent pure.

Braze alloys were prepared by the following procedure. The components of the alloy or compound were carefully weighed out to the nearest milligram and were placed in a vycor or pyrex glass capsule. The capsule was pumped down by a mechanical vacuum pump, backfilled with argon and then pumped down again. A minimum of ten pumping, filling cycles were employed. Following the last pumpdown the capsule was sealed. Each alloy was taken above its melting temperature, removed from the furnace, agitated and reheated at least five times. The capsule was then air cooled to room temperature. Metallographic and visual examination showed that all the alloys were homogeneous and sound except for InSe which could not be successfully prepared in two trials. No further work was performed with this material.

TABLE II

Potential Braze Alloys Selected for this Study

Alloy	Type of Alloy	Melting Point, ^{o}C
SnTe	Compound	790
Bi_2Te_3	Compound	585
InSb	Compound	530
CdSb	Compound	456
InSe	Compound	660
InTe	Compound	696
Sb_2Te_3	Compound	622
AuZn	Compound	725
56% Ag - 44% Sb	Eutectic	485
41% In - 59% Au	Eutectic between AuIn and $AuIn_2$	494
76.5% Sb - 23.5% Cu	Eutectic	526
79.9% Sb - 20.1% Zn	Eutectic	505
70% Sb - 30% Bi	Solid Solution	430
Sn	Elemental	232
Bi	Elemental	271
Se	Elemental	217
Sb	Elemental	631
In	Elemental	157
Cu	Elemental	1083

B. Shoe Materials

Samples of ten prospective shoe materials were procured in sheet form for wettability tests with selected braze alloys. Although the emphasis was placed on non-magnetic materials, conventional shoe materials such as iron and nickel were included for comparative purposes. The materials under study are listed in Table III along with their melting temperatures and coefficients of expansion. In addition, a sample of Carpenter No. 10, a modified austenitic stainless steel, has been ordered for evaluation. This material reportedly retains its non-magnetic properties even after 60 - 80% cold work. The thermal expansion of Carpenter No. 10 is $18.6\,^{\circ}C^{-1}$, almost identical to that of PbTe.

C. Wettability Tests

A preliminary evaluation of braze and shoe materials was performed by checking the wettability of each of the braze materials on PbTe. Those that appeared promising were tested on each of the potential shoe materials. The wettability of each of the shoe materials by PbTe was also checked.

The tests were carried out in a Lindberg globar furnace outfitted with an Inconel muffle and purified argon atmosphere. The incoming gas was dried by passing successively through two condensers immersed in dry ice-acetone baths and was deoxidized by passing over calcium chips at about $400^{\circ}C$. The gas was then passed through a Drierite column before entering the furnace. The resultant argon had a dewpoint of approximately -50° to $-60^{\circ}C$. A schematic of the test setup is shown as Figure 1.

Tests of the wettability of PbTe by various braze materials were carried out in the following manner. For each test wafers of n-PbTe and p-PbTe were placed on an alumina plate. A sample of the braze to be evaluated was placed on top of each wafer and the assembly was carefully inserted into the furnace. The muffle was purged for at least one hour and the sample was then heated until signs of melting of the braze were visually observed through a plexiglas port.

TABLE III

Prospective Shoe Materials Procured for Testing

Alloy	Composition in Wt. Percent	Melting Temp. ^oC	Coef. of Thermal Exp. $^oC^{-1} \times 10^6$
Iron		1537	11.76
Nickel		1453	13.3
Columbium		2468	7.31
Molybdenum		2610	4.9
Beryllium		1277	11.6
304 Stainless Steel	19 Cr, 10 Ni, .08 C, 2 Mn, 1 Si, Bal Fe	1400 - 1455	16.6
Rene' 41	11 Co, 19 Cr, 10 Mo, 5 Fe, 1.5 Al, 3.2 Ti, 0.12 C, Bal Ni	1310 - 1345	13.5
Haynes 25	10 Ni, 20 Cr, 15 W, 3 Fe, 1.5 Mn, 0.10 C, Bal Co	1329 - 1410	12.3
Multimet	20 Ni, 20 Co, 21 Cr, 3 Mo, 2.5 W, 1 Cb + Ta, 1 Si, 1.5 Mn, 0.12 C, Bal Fe	1288 - 1354	14.1
Magnil	18 Cr, 15 Mn, 0.1 C, Bal Fe	-----	17.9
PbTe		917	16 - 19

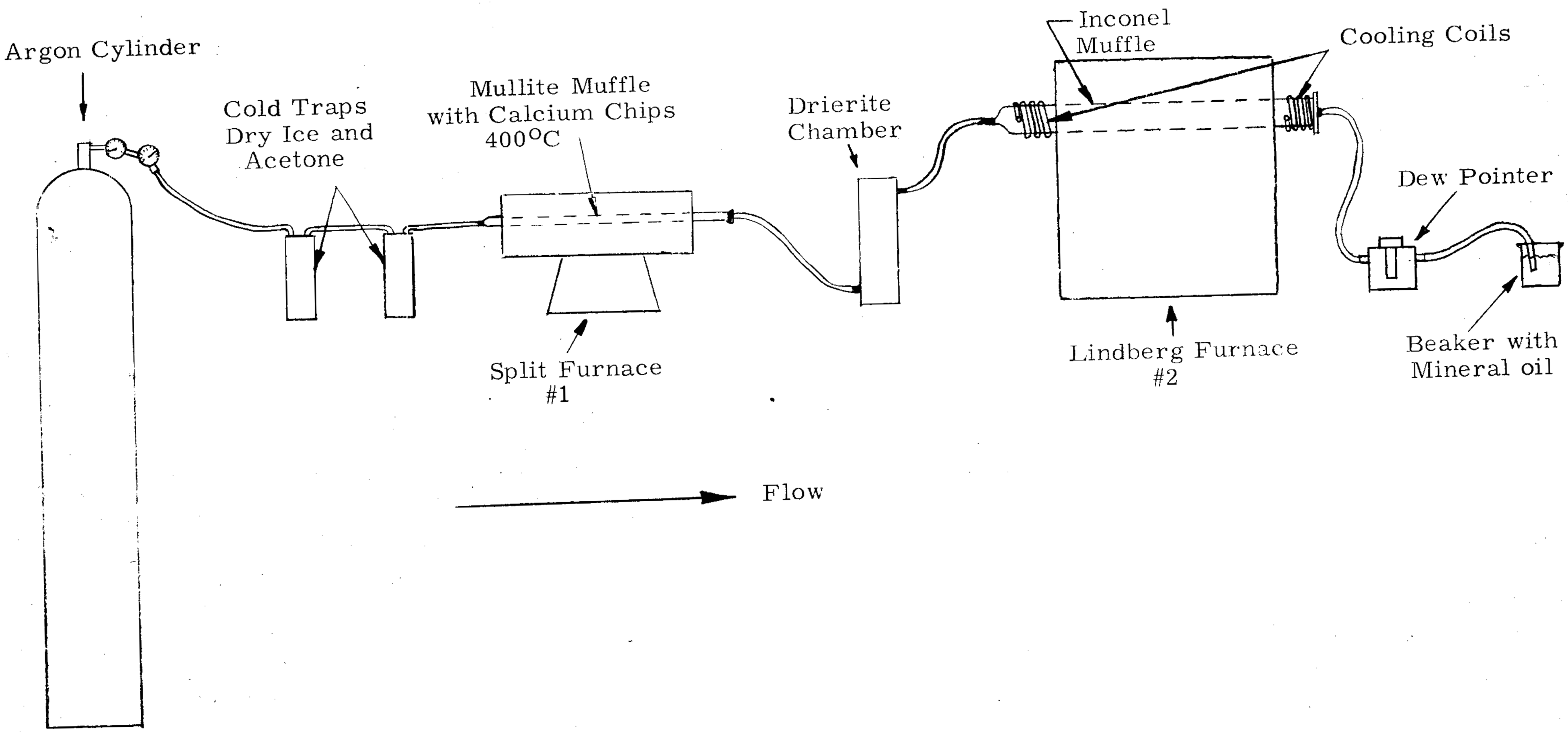

Figure 1. Schematic of Wettability Test Setup

The samples were examined visually and were then cut through the bond with a jeweler's saw and mounted for metallographic examination. Table IV shows the results of these tests and identifies those braze materials chosen for further study.

Choice was made on the basis of test results. However, program limitations made it necessary to remove from further consideration some materials that were of marginal interest. At least one material was chosen from each group, elements, intermetallic compounds, eutectics and solid solutions.

Wettability tests on shoe materials were carried out in a similar manner. In this case sheet samples of nine of the shoe materials (magnil was obtained later and tested separately) were placed on the alumina plate and the braze to be evaluated was placed on each. Test and evaluation procedures were identical with those described above. The results of these tests are reported in Table 5.

In no case was a flux used to aid wetting. Sample preparation consisted of abrasion to remove surface oxides followed by degreasing in acetone. The reported results are indicative but are not conclusive evidence of the bonding that may be obtained by varying the cycle parameters. It is clear that bonding will be more readily attained with the iron, nickel and cobalt base alloys than with beryllium or the refractory metals.

TABLE IV

Wettability of PbTe by Braze Materials

Braze Material	Braze Melting Temp. °C	Max. Test Temp. °C	Results	Chosen for Continued Evaluation
Sn	232	270	poor flow but good adherence	x
Bi	271	300	good flow and adherence	x
Se	217	233	good flow and adherence	
Sb	631	700	poor flow, good wetting	
In	157	192	poor flow, no bond	
Cu	1083	657	entire sample had melted; the 500°C Cu-PbTe eutectic temp. was exceeded	
SnTe	790	860	good flow, excellent wetting; some cracks and pores; retest showed no pores	x
Bi_2Te_3	585	648	excellent flow and wetting; pores in Bi_2Te_3 adjacent to interface	x
InSb	535	525	good flow and wetting; cracks in PbTe	x
CdSb	456	612	braze separated from n-PbTe before mounting; p-PbTe sample had two intermediate phases and poor flow	
InTe	696	747	excellent flow and wetting; some pores and cracks in InTe	x
Sb_2Te_3	622	670	good to excellent flow and wetting; pores in p-PbTe adjacent to interface; signs of cracking or separation in n-PbTe interface	x
AuZn	725	869	no bond formed	

TABLE IV (Cont.)

Braze Material	Braze Melting Temp. °C	Max. Test Temp. °C	Results	Chosen for Continued Evaluation
56% Ag - 44% Sb	485	666	extensive penetration into PbTe; good flow; phase in interface	x
41% In - 59% Au	494	582	poor flow; poor bond	
76.5% Sb - 23.5% Cu	526	673	good flow and wetting	
79.9% Sb - 20.1% Zn	505	649	poor flow; two phases in interface	
70% Sb - 30% Bi	430	665	good flow and wetting; few cracks in PbTe	x

Table V

Summary of Test Results of Brazes on Shoe Materials

Shoe \ Braze	InSb	SnTe	Bi_2Te_3	InTe	Sb_2Te_3
Beryllium	No flow; bond broke with light pressure	No flow; poor bond	Fair flow; poor bond	No flow or bond	No flow or bond
Columbium	Poor flow and bond	No flow; poor bond	Fair flow; poor bond	Poor flow; no bond	Poor flow and bond
Iron	Good flow, no tarnish; broke while sawing	Good flow; bond broke while sawing; reaction zone	Good flow; poor bond, broke while sawing	Poor flow; no bond	Excellent flow; Metallography indicates bond poor
Molybdenum	Poor flow; bond looked good but broke while sawing	Good flow; bond broke while sawing	Fair flow; no bond	Poor flow; no bond	Poor flow; no bond
Nickel	Excellent flow and bond; slight reaction zone	Excellent flow; poor bond	Excellent flow; poor bond	Complete reaction; no sign of nickel	Poor flow and bond
Haynes-25	Poor flow and bond	Excellent flow; good bond; reaction zone	Excellent flow; metallography shows bond poor	Good flow; bond intermittent but good where present	Excellent flow; good bond
Multimet	Poor flow and bond	Very good flow; reaction zone; bond separated	Excellent flow; good bond; reaction zone	Good flow and bond; cracks in InTe away from bond	Excellent flow; metallography shows bond separation
Rene' 41	Poor flow and bond	Good flow; poor bond; reaction zone	Good flow; poor surface appearance	Good flow; poor bond	Very good flow; some bond separation
304 Stainless	Poor flow and bond	Good flow and bond	Excellent flow; good bond	Good flow and bond	Excellent flow; reaction zone; Sb_2-Te_3 cracked
Magnil (.003")	-----------------	Good flow and bond	Good flow; no bond	Poor flow and bond	Bad reaction

Table V (Cont.)

Braze / Shoe	56 w/o Ag - 44 w/o Sb	70 w/o Sb - 30 w/o Bi	Sn	Bi	PbTe
Beryllium	No flow or bond	No flow or bond	No flow or bond	Poor flow; no bond	Fair flow; PbTe cracked; bond poor
Columbium	No flow or bond	No flow or bond	No flow or bond	No flow or bond	Good flow; poor bond
Iron	No flow or bond	No flow or bond	Poor flow; good bond	No flow or bond	Good flow; poor bond
Molybdenum	No flow or bond	No flow or bond	No flow or bond	No flow or bond	Good flow; reaction zone; bond separation
Nickel	No flow or bond	Poor flow and bond	Good flow and bond; reaction zone	Fair flow; good bond	Fair flow; reaction zone; porosity in PbTe
Haynes-25	No flow or bond	No flow; poor bond	No flow or bond	No flow or bond	Good flow; reaction zone; bond separation
Multimet	No flow or bond	No flow or bond	No flow or bond	No flow or bond	Good flow and bond; reaction zone
Rene' 41	No flow or bond	No flow; poor bond	No flow or bond	No flow or bond	Very good flow; cracking in PbTe phase
304 Stainless	No flow or bond	No flow or bond	No flow or bond	No flow or bond	Good flow; poor bond
Magnil (.003")	--------------	--------------	No flow or bond	--------------	--------------

V. POISONING EFFECTS STUDY

There are two serious problems to be overcome in bonding any thermoelectric material to a shoe. First, the bond must be mechanically sound and must remain so throughout its intended lifetime. Second, the diffusion of any elements from the braze or shoe into the thermoelement must not deleteriously affect the thermoelectric properties of the material. The sturdiest bond will be unsatisfactory if the thermoelectric output declines as a result of diffusion from the bond into the elements.

Therefore, before developing bonding procedures, tests were undertaken to determine the effect of diffusion of promising braze and shoe materials on the electric properties of PbTe. In order to magnify any effect, the PbTe thermoelectric elements were uniformly contaminated by the addition of one percent by weight of each material tested. One n-PbTe and one p-PbTe sample containing each contaminant was prepared by the hot pressing technique described in Chapter III.

The following 15 additives were or will be employed in this study:

SnTe	56 w/o Ag - 44 w/o Sb	Ni
Bi_2Te_3	70 w/o Sb - 30 w/o Bi	Fe
InSb	Sn	347 stainless steel
InTe	Bi	Mo
Sb_2Te_3	Cu	Cb

Resistivity and Seebeck coefficient of these samples and of uncontaminated controls were measured on the devices pictured schematically in Figures 2 and 3, respectively. To check the resistivity device, values obtained from our uncontaminated PbTe and for 3M cold-pressed and sintered material were compared with values reported in the literature by 3M. Excellent correlation was achieved. Similarly the Seebeck device was checked by comparing the values obtained in our hot-pressed PbTe samples with those reported by 3M for their cold-pressed and sintered elements prepared from the same starting materials. Again the correlation was excellent. These tests indicate that our sample preparation and test techniques will yield satisfactory results.

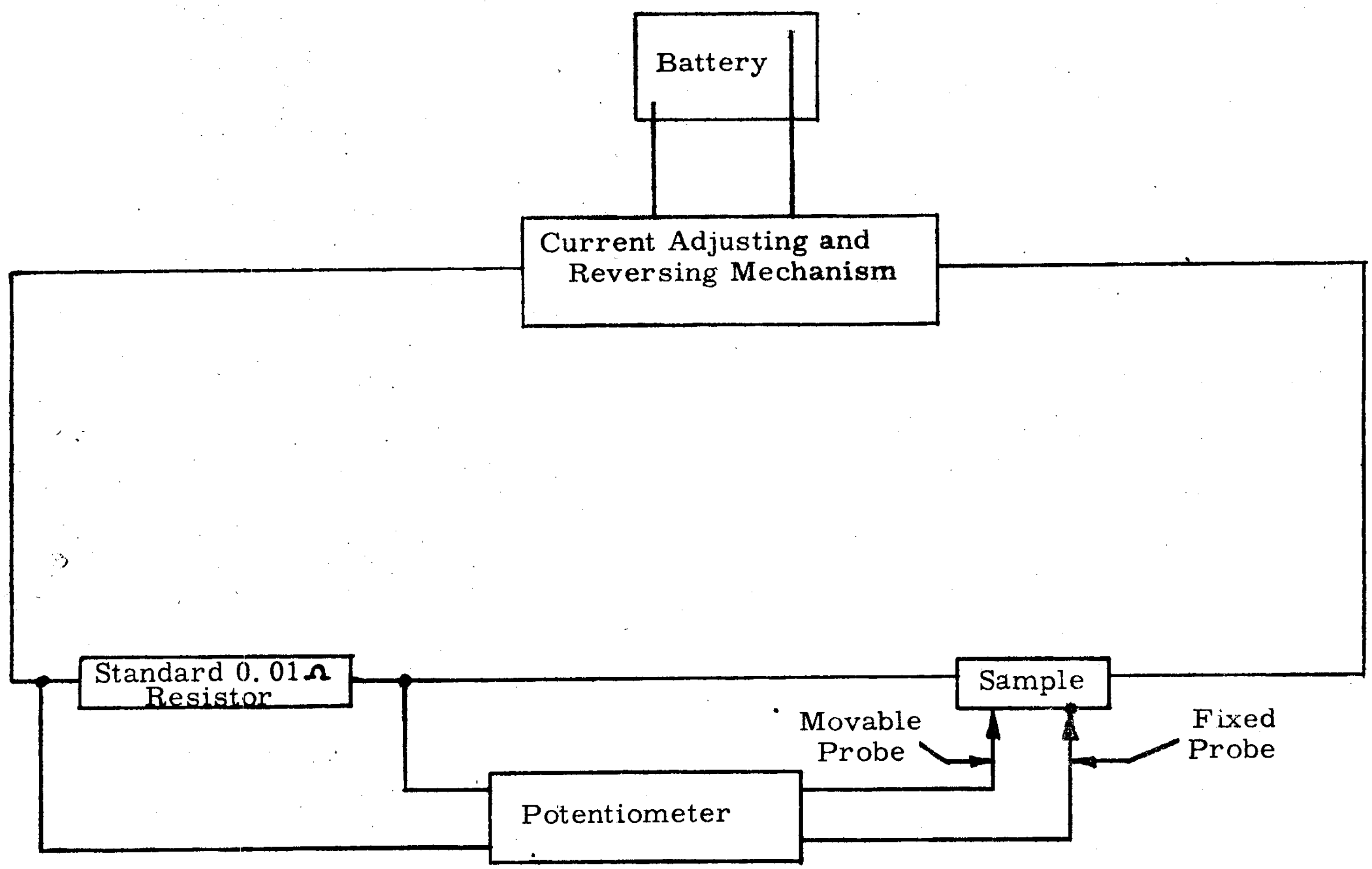

Figure 2. Resistivity Test Schematic

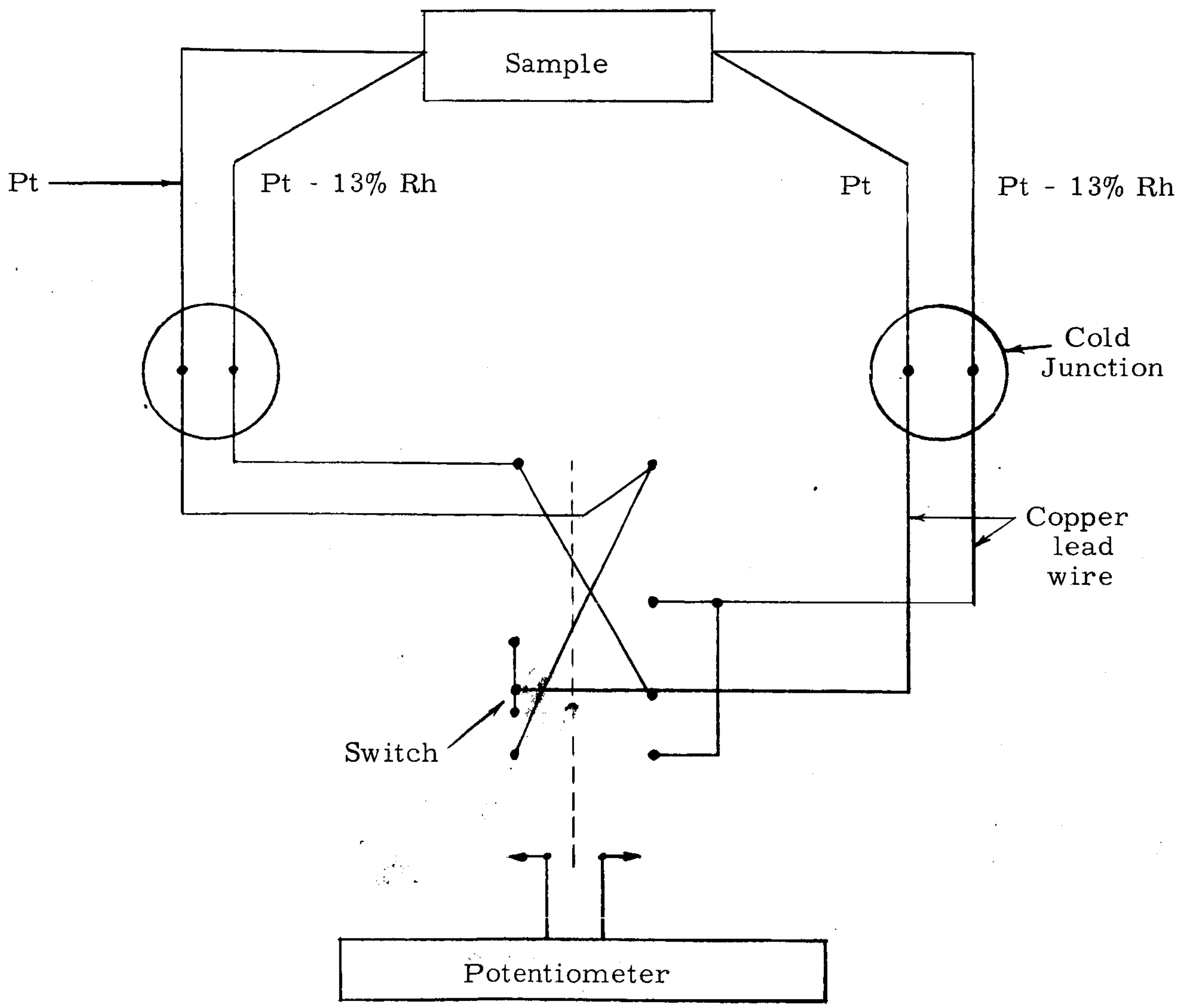

Figure 3. Schematic of Seebeck Test Setup

This phase of the program is not yet complete. The resistivity data taken to date are shown in Table VI and the Seebeck coefficients measured to date are reported in Table VII. Of the four materials for which complete data are available only SnTe is non-poisoning to both p- and n-PbTe. Bi_2Te_3, InTe and Sb_2Te_3 adversely affect the resistivity or Seebeck of one or both lead tellurides.

This work is continuing and is planned for completion during the next quarter.

TABLE VI

Electrical Resistivity Test Results - PbTe Containing 1 w/o Additive
Room Temperature

Additive	Average Resistivity in Microohm Inches[1] n-PbTe	p-PbTe
SnTe	172	350
Bi_2Te_3	123	2570
InSb	785	6275
InTe	799	10000
Sb_2Te_3	94	750
56% Ag - 44% Sb	8600	---
70% Sb - 30% Bi	104	351
Sn	209	2110[2]
Bi	107	353
Cu	87	363
Ni	194	7105[2]
Fe	172	475
374 SS	177	520
Mo	150	156
None	199	129
3M PbTe - no additive	202	188
3M Literature	200	165

(1) Average of two or more measurements.

(2) To be rerun.

TABLE VII

Seebeck Test Results - PbTe Containing 1 w/o Additives

Composition	T_{av}, ^{o}C	Seebeck Coefficient, $\mu V/^{o}C$ Measured	Seebeck Coefficient, $\mu V/^{o}C$ Reported by 3M
n-PbTe	107	-177	-180
	161	-196	-204
n-PbTe + 1 w/o SnTe	108	-175	
	162	-199	
n-PbTe + 1 w/o Bi_2Te_3	106	- 58	
	163	- 76	
n-PbTe + 1 w/o InTe	104	-211	
	155	-249	
n-PbTe + 1 w/o Sb_2Te_3	105	65 Uncertain whether	
	175	82 p or n	
n-PbTe + 1 w/o Ag-Sb	101	-362	
	159	-383	
p-PbTe	100	+105	+104
	109	+109	+116
	148	+148	+140
	159	+139	+148
p-PbTe + 1 w/o SnTe	105	+122	
	159	+162	
p-PbTe + 1 w/o Bi_2Te_3	106	- 63	
	163	- 51	
p-PbTe + 1 w/o InTe	110	+149	
	168	+187	
p-PbTe + 1 w/o Sb_2Te_3	91	+226	
	146	+197	

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